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- 1) South African Patent Application No. 99/3815 accompanied by a Provisional Specification was filed at the South African Patent Office on the 7 June 1999, in the name of **University of Pretoria** in respect of an invention entitled: **"Beneficiation of zircon"**.
- 2) The photocopy attached hereto is a true copy of the provisional specification and drawings filed with South African Patent Application No. 99/3815.

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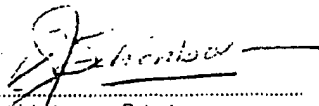
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REPUBLIC OF SOUTH AFRICA  
PATENTS ACT, 1978  
APPLICATION FOR A PATENT AND  
ACKNOWLEDGEMENT OF RECEIPT  
(Section 30(1) Regulation 22)

REPUBLIC OF SOUTH AFRICA  
FORM P.1 - RECEIPT  
(to be lodged in duplicate)

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THE GRANT OF A PATENT IS HEREBY REQUESTED BY THE UNDERMENTIONED APPLICANT  
ON THE BASIS OF THE PRESENT APPLICATION FILED IN DUPLICATE

21 01 PATENT APPLICATION NO 973815

A&A REF V13438 LVDWIT

71 FULL NAME(S) OF APPLICANT(S)

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Pretoria, 0002, Republic of South Africa

54 TITLE OF INVENTION

"BENEFICIATION OF ZIRCON"

Only the items marked with an "X" in the blocks below are applicable.

☐ THE APPLICANT CLAIMS PRIORITY AS SET OUT ON THE ACCOMPANYING FORM P.2. The earliest priority claimed is

Country:

No:

Date:

☐ THE APPLICATION IS FOR A PATENT OF ADDITION TO PATENT APPLICATION NO

21 01

☐ THIS APPLICATION IS A FRESH APPLICATION IN TERMS OF SECTION 37 AND BASED ON  
APPLICATION NO

21 01

THIS APPLICATION IS ACCOMPANIED BY:

- ☒ A single copy of a provisional specification of 28 pages  
☒ Drawings of 1 sheets  
☐ Publication particulars and abstract (Form P.8 in duplicate) (for complete only)  
☐ A copy of Figure of the drawings (if any) for the abstract (for complete only)  
☒ An assignment of invention  
☐ Certified priority document(s). (State quantity)  
☐ Translation of the priority document(s)  
☐ An assignment of priority rights  
☐ A copy of Form P.2 and the specification of RSA Patent Application No  
☒ Form P.2 in duplicate  
☒ A declaration and power of attorney on Form P.3  
☐ Request for ante-dating on Form P.4  
☐ Request for classification on Form P.9  
☐ Request for delay of acceptance on Form P.4  
☐ Extra copy of informal drawings (for complete only)

21 01

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Dated this 7 day of June 1999

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APPLICANTS PATENT ATTORNEYS

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A&A P201

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FORM P6

REPUBLIC OF SOUTH AFRICA  
Patents Act, 1978

## PROVISIONAL SPECIFICATION

(Section 30 (1) - Regulation 27)

21	01	OFFICIAL APPLICATION NO
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993815

22	LODGING DATE
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7 June 1999

71	FULL NAME(S) OF APPLICANT(S)
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UNIVERSITY OF PRETORIA

72	FULL NAME(S) OF INVENTOR(S)
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WILLEM JOHANNES DE WET

54	TITLE OF INVENTION
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"BENEFICIATION OF ZIRCON"

THIS INVENTION relates to the beneficiation of zircon. In particular, it relates to a process for the beneficiation of zircon to produce an upgraded zirconium-containing product or acid zirconium sulphate tetrahydrate, to a process for preparing zirconium basic sulphate from a solution containing acid zirconium sulphate tetrahydrate, to a process for the beneficiation of zircon to produce zircon  
5 derived base material suitable for pigments or opacifier material, and to a method of forming an alkali-fusion decomposed zircon product in a container or reactor.

As a result of dwindling supplies of zirconia as natural baddeleyite, a considerably larger proportion of zirconia and other zirconium products may in future have to be obtained from abundant zircon sands. Such replacement zirconia may be produced from zircon by desilication in a melting furnace, or by thermal plasma dissociation, followed by silica removal by selective chemical dissolution. However, zirconia obtained through the use of both the above thermal technologies still requires chemical purification or processing to obtain the desired physical and  
15 chemical properties for diverse applications.

A problem of growing concern with zircon is its natural radioactivity content with associated occupational health and environmental difficulties, already being experienced by those involved in the fine milling and the destructive processing of zircon, even though its radioactivity content is usually only about

50% of that of acid-leached milled baddeleyite. Waste disposal in zircon processing, as well as final disposal of zircon and related products, are being scrutinized for stricter control for materials with radioactivity equivalents above 10Bec/g. This may lead to licensing requirements for transport and storage of zircon in addition to labelling of transport containers and also to licensing of plants handling zircon materials. The implication of the foregoing is an increased future demand for zirconia and zirconium products of relatively low radioactivity content. This may be achievable through destructive chemical processing, provided such processing, on a sufficiently large scale, can be performed more rapidly and cheaply than the rather tedious conventional approaches.

According to a first aspect of the invention, there is provided a process for the beneficiation of zircon to produce an upgraded zirconium-containing product, the process including

forming an alkali-fusion decomposed zircon product (hereinafter called AFDZ) by mixing the zircon with an alkali and allowing them to react at an elevated temperature;

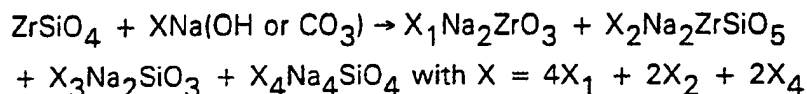
subjecting the AFDZ to a leaching step to provide a liquid phase, and a wet residue which includes at least some of the alkali initially mixed with the zircon;

recovering at least some of the alkali from the wet residue; and

treating the wet residue to produce the upgraded zirconium-containing product.

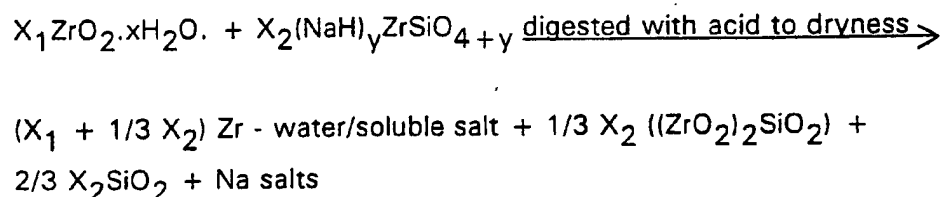
The alkali may be a sodium compound. Preferably, the alkali is NaOH or  $\text{Na}_2\text{CO}_3$ . When the alkali is NaOH, the zircon and NaOH may be allowed to react in a  $\text{CO}_2$ -free atmosphere. As water vapour is released during the reaction of the alkali and the zircon,  $\text{CO}_2$  ingress into a vessel, container, or reactor in which the reaction occurs, is inhibited. It has also been found that a slow stream of air flushed over the contents of a not too tightly covered fusion container prevents  $\text{CO}_2$  uptake.

Without wishing to be bound by theory, the Applicant believes that the alkali-fusion decomposition (desilication) reaction of zircon to form AFDZ can be given as follows (for  $X \geq 2$ ):



Water leachable  $\text{SiO}_2$  values as percentages are then expected to be equal to  $100X_1$ . The Applicant has also found that acid extractable zirconium, as a percentage, is found to be exactly given by  $100(X_1 + \frac{1}{3} X_2)$  for NaOH fusions of zircon at  $650^\circ\text{C}$ . At fusion temperatures of  $850^\circ\text{C}$  more zirconium is acid extractable for all mass ratios of zircon : alkali than is predicted by this equation. For both NaOH and  $\text{Na}_2\text{CO}_3$  fusions a reversal of this trend is found at fusion temperatures of  $1050^\circ\text{C}$ . It is thus clear that towards higher fusion temperatures (above about  $900^\circ\text{C}$ ), the fusion products (AFDZ) of alkali desilication become more complex.

The above equation for the percentage acid extractable zirconium implies that at around a fusion temperature of  $650^\circ\text{C}$ , the acid desilication of water-leached AFDZ takes place accordingly to the following equation:



A dehydrated insoluble residue from the above reaction after water leaching and drying contains  $\text{SiO}_2$  and the product " $(\text{ZrO}_2)_2\text{SiO}_2$ ". The latter product may be considered as being derived from zirconium basic silicate (ZOS), a basic zirconium salt of silicic acid, which dehydrates during drying and calcination

to a mixed phase of  $\text{ZrO}_2$  and  $\text{ZrSiO}_4$  rather than apparently forming an own structural modality.

The zircon and the alkali may be mixed in a mass ratio of zircon : alkali of between 1:0,4 and 1:1,1. When the alkali is  $\text{Na}_2\text{CO}_3$ , the mass ratio is typically between 1:0,4 and 1:0,7, preferably between 1:0,58 and 1:0,66, e.g. about 1:0,65. When the alkali is  $\text{NaOH}$ , the mass ratio is typically between 1 : 0,4 and 1 : 1,1, preferably between 1 : 0,76 and 1 : 1,1, e.g. about 1:1. The elevated temperature at which the zircon and alkali are reacted may be between 450°C and 1300°C. Preferably, the temperature is between 450°C and 1050°C. When the alkali is  $\text{NaOH}$ , the elevated temperature is preferably between 450°C and 900°C, and more preferably between 600°C and 700°C, e.g. about 650°C. When the alkali is  $\text{Na}_2\text{CO}_3$ , the elevated temperature is preferably between 900°C and 1300°C, and more preferably between 950°C and 1100°C, e.g. about 1000°C.

Typically, the zircon is in particulate form when reacting with the alkali, and the method may thus include subjecting raw zircon to a size reduction step to provide zircon of a suitable particle size. For  $\text{NaOH}$  as the alkali, a suitable  $d_{50}$  particle size for the zircon is between 10 $\mu\text{m}$  and 45 $\mu\text{m}$ . For  $\text{Na}_2\text{CO}_3$  as the alkali, a suitable  $d_{50}$  particle size for the zircon is between 5 $\mu\text{m}$  and 10 $\mu\text{m}$ . It has been found that a  $d_{50}$  particle size of about 6,5 $\mu\text{m}$  provides good results for both  $\text{NaOH}$  and  $\text{Na}_2\text{CO}_3$  and that larger average particle sizes require higher fusion or reaction temperatures for  $\text{Na}_2\text{CO}_3$  as the alkali.

Prior to subjecting the AFDZ to the leaching step, the AFDZ may be cooled and comminuted. Preferably, the AFDZ is comminuted to a  $d_{50}$  particle size of less than 1mm, more preferably to a  $d_{50}$  particle size of between 0,2mm and 0,8mm.

The leaching step may be a water leaching or water washing step. When the alkali is  $\text{NaOH}$ , at least some silica present in the AFDZ will be leached

from the AFDZ. Preferably, at least 50% of the silica present in the AFDZ is leached out into the water. More preferably, at least 60% of the silica is leached out into the water, and typically at least 66% of the silica is leached out into the water. Advantageously, sodium silicates or precipitated silicas may be produced from the leachate by methods known to those skilled in the art. However, when the alkali is  $\text{Na}_2\text{CO}_3$ , minimal if any silica is leached from the AFDZ into the water. Furthermore, in this water leaching or water washing step, at least about 70% of the alkali initially mixed with the zircon may be leached from the AFDZ, when the alkali is NaOH. Preferably, at least about 80% of the NaOH is leached out into the water. However, when the alkali is  $\text{Na}_2\text{CO}_3$ , minimal if any alkali is leached from the AFDZ.

When the alkali used is NaOH or  $\text{Na}_2\text{CO}_3$ , recovering at least some of the alkali from the wet residue may include mixing  $\text{NaHCO}_3$  with the wet residue and recovering the alkali in the form of  $\text{Na}_2\text{CO}_3$  from the mixture. The  $\text{NaHCO}_3$  may be mixed in a stoichiometric quantity at room temperature with the alkali present in the wet residue. The  $\text{Na}_2\text{CO}_3$  recovered may be in the form of a concentrated  $\text{Na}_2\text{CO}_3$  solution from which  $\text{Na}_2\text{CO}_3$  may advantageously be precipitated for re-use as the alkali to form AFDZ, or be sold as a byproduct. When the alkali is NaOH, about 20% of the alkali initially used remains attached to the fusion products after water leaching, whereas when  $\text{Na}_2\text{CO}_3$  is used as the alkali, virtually all the alkali is still attached to the fusion products after water leaching. It has been found that, when using sodium bicarbonate, alkali losses of less than 3% can be achieved. As will be appreciated, removal of as much alkali as possible from the wet residue has a further advantage that less or no alkali salts require removal from the wet residue during treatment of the wet residue to produce the upgraded zirconium-containing product.

Treating the wet residue to produce the upgraded zirconium-containing product may include acidifying or neutralising the wet residue to a pH of between



4 and 6. Preferably, hydrochloric acid is used to acidify or neutralise the wet residue.

Treating the wet residue may also include washing the wet residue, e.g. with water, to further reduce the level of alkali, such as sodium salts, present in the wet residue.

The upgraded zirconium-containing product may include acid zirconium sulphate tetrahydrate (hereinafter called AZST). Thus, treating the wet residue may further include converting at least some, preferably all acid extractable zirconium in the wet residue into zirconium basic sulphate (hereinafter called ZBS), and subsequently converting the ZBS into AZST. In one embodiment of the invention, this is achieved by adding a stoichiometric quantity of  $H_2SO_4$  or AZST to the washed, wet residue to convert the acid extractable zirconium to ZBS ( $(ZrO_2)_5(SO_3)_2.5$ ) and thus forming a ZBS-containing residue, and drying the ZBS-containing residue at a temperature of between  $120^\circ C$  and  $180^\circ C$ , e.g. about  $150^\circ C$ . The dried ZBS-containing residue is then purified, e.g. by washing it with a hot ( $80^\circ C$  to  $90^\circ C$ ) HCl solution. Preferably, the HCl solution is in the form of an aqueous mixture of HCl and  $HNO_3$ , in proportions of about 8g of concentrated HCl and 4g of concentrated  $HNO_3$  in a litre of water. The purified ZBS is then converted to AZST, e.g. by mixing it with a stoichiometric quantity of  $H_2SO_4$  to form a wet AZST-containing product. The wet AZST-containing product may be dried or roasted at a temperature of between  $150^\circ C$  and  $400^\circ C$ , e.g. at about  $350^\circ C$ , and the AZST may be extracted with water to form an AZST-containing solution. Iron, uranium and calcium, in particular, are separated to a significant extent using this procedure, which is also suitable for the large scale production of pure zirconium products from AFDZ. Thus, zirconia or other zirconium chemical products may then be prepared from the AZST-containing solution by methods known to those skilled in the art.

An important aspect of the formation of ZBS as described above is the non-costly subsequent containment for disposal of separated impurity elements, including radioactive elements. The acid wash solutions (pH approximately 1) from the purification of the ZBS may be treated with a small quantity of ferric sulphate (in roughly twice equivalent amounts to that of the total impurities), heated and then made alkaline, preferably with ammonia, to a pH of greater than 10. Virtually all the impurity elements are thus brought down as a small volume precipitate which may be easily separated from the supernatant solution. The precipitate may be mixed with just enough lime to render an almost dry product, which can be calcined, if desired, for disposal. Furthermore, the final washes used to further reduce the level of alkali in the wet residue as described above may also be added to the acid wash solutions from the ZBS purification, before the impurity elements are precipitated. The separated supernatant solutions may be directly disposed of.

Instead of treating the wet residue to convert acid extractable zirconium into ZBS, and then converting the ZBS into AZST, treating the wet residue may include converting at least some, preferably all acid extractable zirconium in the wet residue into AZST without first converting it into ZBS. This may be effected by mixing a substantially stoichiometric quantity of  $H_2SO_4$  with the wet residue to form an AZST-containing product. The AZST-containing product may be further treated as hereinbefore described or purified as hereinafter described.

It has been found that for NaOH as the alkali, for increasing reaction or fusion temperatures between 650°C and 850°C, increasing proportions of the zirconium in the zircon is acid extractable. For example, at a reaction of fusion temperature of 850°C, using NaOH as the alkali in a mass ratio of 1:1 to the zircon, about 88% of the zirconium is acid extractable, whereas at 650°C about 78% of the zirconium is acid extractable. However, as will be appreciated, from a practical point of view, a fusion or reaction temperature of about 650°C is more

attractive, particularly if heating by fossil or production gaseous fuels are contemplated.

According to a second aspect of the invention, there is provided a process for the beneficiation of zircon to produce AZST, the process including

5 forming AFDZ by mixing the zircon with an alkali and allowing them to react at an elevated temperature;

subjecting the AFDZ to a leaching step to provide a liquid phase, and a wet residue which includes at least some of the alkali and acid extractable zirconium;

removing at least some of the alkali from the wet residue; and

10 converting at least some of the acid extractable zirconium in the wet residue into AZST without first converting it into ZBS, by mixing  $H_2SO_4$  with the wet residue, thus forming an AZST-containing product, the  $H_2SO_4$  being mixed in a molar ratio to the acid extractable zirconium of more than 1,4 : 1, but not more than 2,05 : 1.

15 Preferably, the molar ratio of  $H_2SO_4$  to acid extractable zirconium is about 2 : 1.

In contrast to sulphuric acid (or equivalent sulphation reactants such as  $(NH_4)_2SO_4$ ,  $(NH_4)HSO_4$ ,  $NaHSO_4$ , etc.) dissolution of zirconium from finely milled plasma dissociated zircon or finely milled fused zirconia produced in melting  
20 furnaces, which require high roasting temperatures (300 - 450°C) with equivalent acid ratios in considerable excess of stoichiometric requirements, as well as extended roasting times, concentrated sulphuric acid easily dissolves the acid extractable zirconium from water-leached solid AFDZ residues, even at room temperature. The same is true with concentrated HCl, yielding zirconyl chlorides.  
25 With sulphuric acid even at 350°C, virtually no acid fumes is generated and stoichiometric conversion results to form a dehydrated AZST. Acid zirconium sulphate tetrahydrate (AZST) is thus directly obtainable from the latter after

dissolution in water and separation from insoluble residues, by spray drying or by crystallisation after removal of excess water through evaporation.

5 The process may include roasting the AZST-containing product, e.g. at a temperature of between 150°C and 400°C, preferably about 350°C, until it is dry.

10 The process may include extracting the AZST from the AZST-containing product. In one embodiment of the invention, this is achieved by dissolving the dry AZST-containing product in water to form an AZST-containing solution, and obtaining AZST from the AZST-containing solution by evaporation of excess water and crystallisation, as mentioned hereinbefore. As will be appreciated, the AZST thus contained is impure, but may be acceptable in many applications. Instead, the AZST-containing product may be purified as hereinafter described. As mentioned hereinbefore, zirconia or other zirconium chemical products may also be prepared from the AZST-containing solution by methods  
15 known to those skilled in the art.

To purify the AZST, several known approaches are available, e.g. precipitation with  $\text{NH}_3$  at a pH of about 2.5 from an AZST solution containing about 190g/l of equivalent zirconia. Precipitation is, however, sluggish and long times should be allowed to obtain yields of 80% or more. AZST may also be  
20 evaporated to almost dryness, dissolved in the minimum of water and then precipitated by sulphuric acid addition to a concentration of 65%. Removal of impurities is, however, incomplete, erratic and losses of equivalent zirconia occur. Ion exchange and solvent extraction methods may also be used for purifying AZST solutions.

25 The AFDZ may be formed, and leached, as hereinbefore described. Removing at least some of the alkali from the wet residue may include recovering at least some of the alkali from the wet residue, as hereinbefore described. The

process may include subjecting raw zircon to a size reduction step as hereinbefore described.

According to a third aspect of the invention, there is provided a process for preparing ZBS from a starting solution containing AZST, the process including

precipitating zirconium basic carbonate (hereinafter called ZBC) and soluble sulphates from a portion of the AZST-containing starting solution;

washing the ZBC precipitate until it is substantially free of soluble sulphates; and

mixing the washed ZBC precipitate with the remainder of the AZST-containing starting solution to form a ZBS-containing slurry or product.

The portion of the AZST-containing starting solution from which the ZBC is precipitated is typically about 70% to 80%, with the remainder of the AZST-containing solution mixed with the washed ZBC precipitate thus typically being about 30% to 20% of the starting solution.

Precipitating ZBC from the portion of the AZST-containing starting solution may be effected by admixing  $\text{Na}_2\text{CO}_3$  or  $(\text{NH}_4)_2\text{CO}_3$ , in solution form, to the portion of the AZST-containing solution. A final pH of the admixture may be between 6.5 and 7, e.g. about 6.75.

The ZBC precipitate is typically washed with water.

The process may include vigorously stirring the mixture of ZBC precipitate and the remainder of the AZST-containing starting solution, and heating the mixture e.g. to a temperature of between 70°C and 80°C. Preferably, the mixture is maintained at this temperature for about 10 minutes.

The process may include drying the ZBS-containing slurry, e.g. at a temperature of about 150°C.

The process may also include purifying the ZBS with acid as hereinbefore described. The process may further include converting the purified  
5 ZBS into AZST as hereinbefore described. Thus, the process may be used to provide a purified AZST from a starting solution containing AZST.

According to a fourth aspect of the invention, there is provided a process for producing zircon-derived base material suitable for pigments, the process including

10 forming AFDZ by mixing the zircon with an alkali and allowing it to react at an elevated temperature;

subjecting the AFDZ to a washing step to reduce the level of alkali salts present in the AFDZ, thereby providing an alkali salt-containing liquid phase, and a wet residue which includes acid extractable zirconium;

15 converting at least some of the acid extractable zirconium in the wet residue into ZBS; and

drying the wet residue and calcining the dried residue to form a calcined product which is a zircon derived base material suitable for pigments.

The AFDZ may be formed as hereinbefore described.

20 During the washing step, some silica present in the zircon may be leached from the AFDZ, particularly if the alkali is NaOH. The process may thus include mixing particulate silica with the calcined product to replenish at least some of the silica leached from the AFDZ. Typically, the zirconium-derived base material includes 50% by mass silica.

If necessary, the process may include a size reduction step, e.g. wet milling, to reduce the average particle size of the wet residue so that it is suitable for pigments, prior to drying and calcining the wet residue.

5 Drying of the wet residue may be effected at an elevated temperature of between 110°C and 150°C, e.g. about 120°C.

Calcining of the dried residue may be effected at a temperature of between 800°C and 1000°C, e.g. about 900°C.

10 The washing step may include mixing the AFDZ with  $\text{NaHCO}_3$  and water, the alkali salt in the alkali salt-containing liquid thus being  $\text{Na}_2\text{CO}_3$ . In this case, no or very little silica is washed or leached from the AFDZ, a wet residue which is produced thus containing substantially all of the silica that was present in the AFDZ. Preferably, at least 90% of the alkali salts present in the AFDZ is leached or washed from the AFDZ. More preferably, at least 95%, and typically at least 97% of the alkali salts present in the AFDZ is leached or washed from the  
15 AFDZ.

The base material is suitable for all zircon-type zirconium pigments, including V-blue, Pr-yellow and Fe-pink pigments.

20 If the acid extractable zirconium in the wet residue is converted into in situ zirconium basic sulphate (ZBS) in the absence of any sodium salts, the formation of a mixed-phase structure upon calcination to 900°C is prevented, as confirmed by Raman spectroscopy. The acid extractable zirconium is converted into a prominently monoclinical zirconia form after calcination (typical composition (w%) 75%  $\text{ZrO}_2$ , 15%  $\text{ZrSiO}_4$  and 10%  $\text{SiO}_2$ ), when about 50% of the silica is leached from the AFDZ during the washing step, which permits the formation of  
25 greatly improved zirconium pigment colours, such as V-blue pigment colours. When no or very little silica is leached from the AFDZ, the mixed phase structure

of the calcined base material has a typical composition by mass of about 58%  $\text{ZrO}_2$ , 13%  $\text{ZrO}_2\text{SiO}_2$  and 29%  $\text{SiO}_2$ . This approach has the advantage of not necessarily having to add any further silica to the calcined material.

5                   Pigments may be prepared from the zircon-derived base material using any suitable method known to those skilled in the art.

                  The process may include recovering at least some of the alkali from the wet residue as hereinbefore described, when the washing step does not include mixing the AFDZ with  $\text{NaHCO}_3$ . The process may instead include recovering at least some of the alkali from the alkali-salt containing liquid when the washing step  
10                   includes mixing the AFDZ with  $\text{NaHCO}_3$ . The process may include subjecting raw zircon to a size reduction step as hereinbefore described.

                  According to a fifth aspect of the invention, there is provided a process for the beneficiation of zircon to produce opacifier material, the process including

15                   forming AFDZ by mixing the zircon with an alkali and allowing them to react at an elevated temperature;

                  subjecting the AFDZ to a leaching step to provide a liquid phase and a wet residue which includes acid extractable zirconium;

20                   treating the wet residue to convert at least some of the acid extractable zirconium in the wet residue into ZBS, thus forming a ZBS-containing product;

                  purifying the ZBS-containing product; and

                  calcining the ZBS-containing product thereby to produce opacifier material.

                  If desired, the process may include subjecting the opacifier material to a size reduction step, e.g. wet milling, to achieve a  $d_{50}$  particle size of less than  
25                    $1,5\mu\text{m}$ . If wet milling is used, the opacifier material may subsequently be dried at a temperature of about  $120^\circ\text{C}$ .



Treating the wet residue to convert the acid extractable zirconium in the wet residue into ZBS may be effected as hereinbefore described. Purifying the ZBS-containing product may be effected as hereinbefore described.

The AFDZ may be formed, and leached, as hereinbefore described.

- 5 The process may include recovering at least some of the alkali from the wet residue as hereinbefore described. The process may include subjecting raw zircon to a size reduction step as hereinbefore described.

According to a sixth aspect of the invention, there is provided a method of forming AFDZ in a container or reactor, the method including

- 10 lining interior wall surfaces of the container or reactor with AFDZ;  
placing a mixture of zircon and an alkali inside the container or reactor so that the AFDZ lining is between the mixture and the interior wall surfaces of the container or reactor; and  
allowing the mixture to react at an elevated temperature to form AFDZ.

- 15 Lining interior wall surfaces of the container or reactor may be effected by means of a suitable jig, which is then withdrawn prior to allowing the mixture to react at an elevated temperature.

- 20 Preferably, the AFDZ lining is between 3mm and 8mm thick. Most preferably, the AFDZ lining is about 5mm thick. However, it is to be appreciated that the AFDZ lining thickness may vary depending on the size of the container or reactor, and may thus fall outside the range provided above.

Preferably, for elevated temperatures above 650°C, the AFDZ in the lining is water leached and comminuted.

The invention will now be described, by way of example, with reference to the accompanying diagrammatic drawing, in which the single figure shows a schematic flow diagram of a process in accordance with the invention.

5 Referring to the drawing, reference numeral 10 generally indicates a process in accordance with the invention for the beneficiation of zircon to produce upgraded zirconium-containing products.

10 The process 10 includes a raw zircon solids feed line 12 leading to a milling stage 14, with a solids discharge line 16 leading to a reaction stage 18. From the reaction stage 18 an AFDZ feed line feeds a cooling and comminuting stage 22 from which a comminuted AFDZ feed line 24 leads to a leaching stage 26. A leachate treating stage 30 is connected by a leachate line 28 to the leaching stage 26, and an alkali recovery stage 34 is connected to the leaching stage 36 by means of a wet residue line 32.

15 An alkali depleted wet residue line 36 leads from the alkali recovery stage 34 to a neutralising stage 38 from where a neutralised wet residue line 40 feeds into a water washing stage 42. The water washing stage 42 is connected to a ZBS producing stage 46 by means of a washed wet residue line 44. A ZBS-containing product line 48 leads from the ZBS producing stage 46 to a drying/roasting stage 50, which is connected to an acid leaching stage 54 by means of a dry ZBS-containing product line 52.

20

An acid leached ZBS-containing product line 56 leads from the acid leaching stage 54 to an AZST producing stage 58. An AZST product containing line 60 leads to an AZST drying stage 62 which is connected to an AZST water extraction stage 66 by means of a dry AZST line 64. An AZST solution product line 68 leads from the AZST water extraction stage 66.

25

As shown in the drawing, the neutralised wet residue line 40 also leads to an in situ AZST producing stage 70 which is connected to an AZST drying/roasting stage 74 by means of an AZST containing product line 72. A dry AZST line 76 leads to a water extraction stage 78 which is connected to a ZBC precipitating stage 84 by means of an AZST solution line 82. The ZBC precipitating stage 84 has a ZBC containing product line 86 leading to a precipitate washing stage 88 from where a washed precipitate line 90 leads to a ZBC/AZST admixing stage 92. A ZBS slurry line 94 leads from the ZBC/AZST admixing stage 92 to a slurry drying stage 96 from where a dry slurry line 98 leads to an acid leaching stage 100. A leached ZBS product line 102 leads from the acid leaching stage 100 to an AZST producing stage 104, with an AZST product line leading from the AZST producing stage 104.

The ZBS-containing product line 48 also leads to a wet residue milling stage 108, from which a wet milled residue line 110 leads to a drying/calcining stage 112. A calcined product line 114 leads from the drying/calcining stage 112 to a fine silica mixing stage 116 from which a zircon base material product line 118 leads.

The acid leached ZBS containing product line 56 also leads to a calcining stage 120 and to the wet residue milling stage 108. A calcined product line 122 leads from the calcining stage 120 to a wet milling stage 124, from which an opacifier product line 126 leads.

In accordance with the process 10, raw zircon solids is fed along the raw zircon solids feed line 12 to the milling stage 14, where it is milled to have an appropriate  $d_{50}$  particle size. The milled zircon is discharged through the solids discharge line 16 to the reaction stage 18, where it is mixed with  $\text{Na}_2\text{CO}_3$  and allowed to react at an elevated temperature of about  $1000^\circ\text{C}$  to form AFDZ. A mass ratio between the zircon and the  $\text{Na}_2\text{CO}_3$  is about 1:0,65. The AFDZ is fed along the AFDZ feed line 20 to the cooling and comminuting stage 22, where the

AFDZ is cooled down and comminuted to a  $d_{50}$  particle size of less than 1mm. The cooled, comminuted AFDZ is fed along the comminuted AFDZ feed line 24 to the leaching stage 26, where it is leached with water. In the leaching stage 26, minimal silica and  $\text{Na}_2\text{CO}_3$  is leached from the AFDZ. Instead of using  $\text{Na}_2\text{CO}_3$  in the reaction stage 18, NaOH may be used in a mass ratio of zircon : NaOH of about 1 : 1,1. In this case, the reaction takes place at about 650°C, and about 66% of the silica and about 80% of the NaOH are leached from the AFDZ into the water. Leachate from the leaching stage 26 passes along the leachate line 28 to the leachate treating stage 30, where sodium silicates and/or precipitated silicas are produced from the leachate by methods known to those skilled in the art.

Wet residue from the leaching stage 26 is passed along the wet residue line 32 to the alkali recovery stage 34, where it is mixed at room temperature with  $\text{NaHCO}_3$  to recover  $\text{Na}_2\text{CO}_3$ , in the form of a concentrated solution, from the wet residue leaving an alkali-depleted wet residue. The  $\text{Na}_2\text{CO}_3$  can be precipitated and reused as the alkali in the reaction stage 18.

The alkali depleted wet residue leaves the alkali recovery stage 34 along the alkali depleted wet residue line 36 and enters the neutralising stage 38, where it is neutralised with HCl to a pH of about 5. Neutralised wet residue thus leaves the neutralising stage 38 along the neutralised wet residue line 40 and is passed to the water washing stage 42 for removal of sodium salts from the alkali depleted wet residue.

The washed wet residue is fed by means of the washed wet residue line 44 into the ZBS producing stage 46, where a calculated stoichiometric quantity of  $\text{H}_2\text{SO}_4$  (or AZST) is added to the wet residue to convert acid extractable zirconium in the wet residue into ZBS. A ZBS containing product is thus passed along the ZBS containing product line 48 to the drying/roasting stage 50, where the ZBS containing product is dried at a temperature of about 150°C. The dried ZBS containing product moves along the dry ZBS containing product line 52 to the

acid leaching stage 54, where the dry ZBS containing product is leached with an aqueous mixture of HCl and HNO<sub>3</sub> in proportions of about 8g of concentrated HCl and 4g of concentrated HNO<sub>3</sub> in a litre of water. The aqueous acid mixture is at a temperature of about 85°C.

5                   An acid leached ZBS containing product thus feeds into the AZST producing stage 58 by means of the acid leached ZBS containing product line 56. In the AZST producing stage 58, the acid leached ZBS containing product is treated with a calculated stoichiometric quantity of H<sub>2</sub>SO<sub>4</sub> to convert the ZBS into AZST. The AZST is passed along the AZST product containing line 60 to the  
10                   AZST drying stage 62 where it is dried at a temperature of about 350°C. The dry AZST moves along the dry AZST line 64 to the AZST water extraction stage 66, where the dry AZST is extracted with water to form an AZST solution product which is delivered through the AZST solution product line 68. The AZST solution may be further treated by methods known to those skilled in the art, to produce  
15                   zirconia or other zirconium chemical products.

                  Instead of going to the water washing stage 42, some or all of the neutralised wet residue from the neutralising stage 38 may be passed to the in situ AZST producing stage 70. In the in situ AZST producing stage 70 a calculated  
20                   stoichiometric quantity of H<sub>2</sub>SO<sub>4</sub> is added to the neutralised wet residue to convert acid extractable zirconium in the wet residue directly into AZST. The molar ratio of the H<sub>2</sub>SO<sub>4</sub> to the acid extractable zirconium is about 2 : 1. An AZST containing product is thus passed along the AZST containing product line 72 to the AZST drying/roasting stage 74, where the AZST containing product is roasted at a temperature of about 350°C. Dry AZST is fed along the dry AZST  
25                   line 76 to the water extraction stage 78, where the AZST is extracted from the solids into the water to form an AZST containing solution.

                  The AZST containing solution may then be further treated/purified by passing it along the AZST solution line 82 to the ZBC precipitating stage 84. In

the ZBC precipitating stage 84, about 75% of the AZST solution is mixed with either a  $\text{Na}_2\text{CO}_3$  solution or an  $(\text{NH}_4)_2\text{CO}_3$  solution to obtain a final solution pH of about 6.75, thus precipitating ZBC and soluble sulphates from the solution. A ZBC containing product is then passed along the ZBC containing product line 86 to the precipitate washing stage 88, where the ZBC containing product or precipitate is washed thoroughly with water until it is free of soluble sulphates. The washed precipitate is passed along the washed precipitate line 90 to the ZBC/AZST admixing stage 92, where the remaining 25% of the AZST containing solution is vigorously stirred up with the ZBC containing precipitate and heated to a temperature of about  $75^\circ\text{C}$  for a period of about 10 minutes, thus forming a ZBS slurry.

The ZBS slurry is passed along the ZBS slurry line 94 to the slurry drying stage 96 where it is dried at a temperature of about  $150^\circ\text{C}$ , whereafter it is fed to the acid leaching stage 100 along the dry slurry line 98. In the acid leaching stage 100, the ZBS product is treated in the same way as in the acid leaching stage 54, with a leached ZBS product thus being fed along the leached ZBS product line 102 to the AZST producing stage 104. In the AZST producing stage 104, AZST is produced in the same fashion as in the AZST producing stage 58, to produce an AZST product delivered through the AZST product line 106. The AZST product may be further treated if desired.

If it is desired to produce zircon derived base material suitable for pigments using the process 10, some or all of the ZBS-containing product (which is in the form of a wet residue) from the ZBS-producing stage 46 is passed along the ZBS-containing product line 48 to the wet residue milling stage 108, where the wet residue is wet milled to have an average particle size which is appropriate for pigments. Alternatively, acid leached ZBS-containing product from the acid leaching stage 54 is fed to the wet residue milling stage 108. As will be appreciated, if the alkali used in the reaction stage 18 is  $\text{NaOH}$  and not  $\text{Na}_2\text{CO}_3$ ,

at least 50% of the silica in the AFDZ is leached from the AFDZ in the leaching stage 26.

The milled residue is fed along the wet milled residue line 110 to the drying/calcining stage 112, where it is initially dried at a temperature of about 120°C, and then calcined at a temperature of about 900°C. The calcined product is thus fed along the calcined product line 114 to the fine silica mixing stage 116. In the fine silica mixing stage 116, the calcined product is mixed with fine particulate silica to replenish the silica initially leached from the AFDZ in the leaching stage 26. Zircon derived base material is thus delivered through the zircon derived base material product line 118 and can be used to prepare zirconium pigment.

In a variation of the above process for producing zircon-type base material suitable for pigments, the AFDZ from the cooling and comminuting stage 22 is mixed with  $\text{NaHCO}_3$  and water in a washing stage 128, forming a  $\text{Na}_2\text{CO}_3$ -containing liquid and a wet residue. The wet residue thus contains substantially all of the silica that was present in the AFDZ, and the  $\text{Na}_2\text{CO}_3$ -containing liquid includes 95% of the alkali salts, as  $\text{Na}_2\text{CO}_3$ , that were present in the AFDZ. The wet residue is then passed to the ZBS producing stage 46, from where the ZBS-containing product is fed to the wet residue milling stage 108 and the drying/calcining stage 112.

It will typically not be necessary to add fine silica to the calcined product, which is thus a zircon-derived base material suitable for zirconium pigment.

In order to produce opacifier material using the process 10 of the invention, acid leached ZBS containing product is fed along the acid leached ZBS containing product line 56 to the calcining stage 120 where it is calcined at a temperature of about 900°C. Calcined product passes along the calcined product

line 122 to the wet milling stage 124, where the calcined product is wet milled to achieve a  $d_{50}$  particle size of less than  $1.5\mu\text{m}$ . Thus, opacifier material is discharged through the opacifier product line 126 and may thereafter be dried at a temperature of about  $120^{\circ}\text{C}$  in a drying stage (not shown).

5                    The invention is further illustrated by the following non-limiting examples:

#### EXAMPLE 1

AFDZ was prepared using zircon powder with a  $d_{50}$  particle size of  $6.5\mu\text{m}$ , using the fusion or reaction conditions listed in Table 1. In all instances a fusion time of 90 minutes was used. The AFDZ was cooled down before  
10                    comminuting the solids to a particle size  $< 1\text{mm}$ . The comminuted AFDZ product for each run was individually water-leached and the water phases and solid wet residues were treated as follows: for measuring the percentages of alkali water-extracted, the water phases were individually titrated with a standardised HCl  
15                    solution with methyl orange as indicator. The percentages of alkali extracted, are given in Table 1. The neutralised solutions after the titrations were subsequently slightly acidified with HCl and then made alkaline with  $\text{NH}_3$  to pH values of  $> 10$  for complete precipitation of their silica contents. The precipitates were separated, washed, dried and finally calcined at about  $750^{\circ}\text{C}$ . The percentages of the silica  
20                    water-extracted from various fusions products, are also given in Table 1.

To determine the percentages of acid extractable zirconium in the various AFDZ samples, their wet residues (after water extraction) were each treated with 20g concentrated sulphuric acid per 18.3g of initial zircon used in the fusions, dried and then roasted at about  $350^{\circ}\text{C}$ . From the roasted products the  
25                    AZST formed were water-leached and the solutions separated from the remaining solid residues. The AZST solutions were all evaporated to dryness and solid AZST products calcined at  $900^{\circ}\text{C}$  for 2 hours to  $\text{ZrO}_2$  products and weighed.



The remaining solid residues from which the AZST solutions were separated, were also dried and then calcined, also at 900°C for 2 hours. The percentages of acid extractable zirconium, also given in Table 1, were calculated from the  $ZrO_2$  masses obtained. Good overall mass balance were found.

**TABLE 1**

Leachate values, in percentages extracted, of alkali and silica extracted with water and zirconium extracted with  $H_2SO_4$  from alkali-fusion decomposed zircon with sodium hydroxide and sodium carbonate as the alkali at various fusion or reaction temperatures and zircon : alkali mass ratios.

Fusion temperature	650°C			850°C			1050°C		
Zircon : alkali mass ratio and alkali used	Component Extracted (%)								
	NaOH	SiO <sub>2</sub>	Zr	NaOH	SiO <sub>2</sub>	Zr	NaOH	SiO <sub>2</sub>	Zr
1.1 (NaOH)	80	63	77.5	85	70	88	-	-	-
0.87 (NaOH)	80	57	71.5	75	63	86	55	42	53.2
0.66 (NaOH)	80	42	58.2	60	45	77	33	13	57
0.44 (NaOH)	80	22	48.2	45	18	68	18	2.5	68.8
0.66 (Na <sub>2</sub> CO <sub>3</sub> )	-	-	-	-	-	-	minimal	minimal	62

**EXAMPLE 2**

AFDZ was prepared using zircon powder with a  $d_{50}$  particle size of  $6.5\mu m$ , using the fusion or reaction conditions note below in Table II. The AFDZ was cooled, comminuted to a particle size of less than 1mm and water leached to provide a water phase and a wet residue. The wet residue was treated with

$\text{NaHCO}_3$  to recover  $\text{Na}_2\text{CO}_3$ , in solution form, therefrom, whereafter the wet residue was neutralised with HCl using methyl orange as an indicator (colour change from yellow to red). The wet residue was washed with water to remove sodium salts.  $\text{H}_2\text{SO}_4$  was added in a stoichiometric quantity to the wet residue

5 to convert acid extractable zirconium in the wet residue into ZBS. Following the in situ precipitation of ZBS the wet residue was oven dried at  $150^\circ\text{C}$ , ground and then twice acid washed with 150ml of each acid solution (containing 8g concentrated HCl and 4g concentrated  $\text{HNO}_3$  in a litre of water. Additional  $\text{H}_2\text{SO}_4$  was added to form AZST from the in situ ZBS before roasting for 1 hour at  $350^\circ\text{C}$ .

10 The AZST was dissolved in  $\text{H}_2\text{O}$ , dried and then calcined to  $\text{ZrO}_2$  at  $900^\circ\text{C}$  for 2 hours before XRF analysis.  $\text{ZrO}_2$  yield was approximately 68%. The results obtained are given in Table II, column a. In column b of Table II, the analysis is given for  $\text{ZrO}_2$  derived from the same AFDZ material but following a conventional route of zirconyl chloride from which ZBS is precipitated using  $(\text{NH}_4)_2\text{SO}_4$  as

15 precipitating agent. The ZBS was separated, washed with water, then dried, calcined to  $\text{ZrO}_2$  at  $900^\circ\text{C}$  and also analysed by XRF. The yield was the same as for the in situ ZBS procedure above.

An AZST solution was prepared from the AZST obtained from the in situ ZBS route above. The solution was adjusted to 6 N HCl and then passed

20 through a pre-equilibrated (with 2N  $\text{H}_2\text{SO}_4$ /6N HCl solution) strong anion exchange resin column (resin Duolite A161L Code 60393, obtained from Rohm and Haas, South Africa (Pty) Ltd). The eluate was dried and then calcined at  $900^\circ\text{C}$ . Instead

of a column separation, a single batch equilibrium was also done with pre-equilibrated strong anion exchange resin (10g resin/AZST derived from 18.3g original zircon used). After 5 minutes stirring, phases were separated and the solution dried and then calcined at 900°C. The XRF analyses for these further purifications are given in columns c and d, respectively, of Table II, from which it is clear that such further purifications are hardly necessary.

TABLE 2

Comparison of the compositions of zirconium products obtainable from alkali-fused zircon by the in situ ZBS process involving acid leaching with that obtained from a conventional process involving precipitation of ZBS from zirconyl chloride. The purities after purification of AZST zirconium products, using strong anion exchange resins, are also given. The purity of  $ZrO_2$  obtained from ZBS (derived from in situ AZST) after purification is given as well as that of an opacifier derived from the in situ ZBS process.

XRF analyses of $ZrO_2$ products derived from the various experiments and also of a purified opacifier.						
Component	a	b	c	d	e	f
$ZrO_2/HfO_2$	99.5%	99.0%	99.5%	99.5%	99.5%	78.95%
$SiO_2$	<0.4%	0.65%	<0.2%	<0.4%	<0.45%	21.09%
Ti ppm	710	633	235	699	278	694
Fe ppm	250	§	§	87	206	108
Ca ppm	<60	276	<30	65	127	100
P ppm	234	608	213	236	289	240

U ppm	40	§ <10	§ <18	<24	<20	81
Th ppm	131	<24	120	121	109	105

The zircon : alkali mass ratio for all the experiments was 0.87 and the fusion temperature 650°C. NaOH was used as alkali. The composition of the milled zircon starting material was as follows:  $\text{ZrO}_2 + \text{HfO}_2$ :65.7%,  $\text{SiO}_2$ :33.6%, ppm Ti:738, ppm Fe:683, ppm Ca:666, ppm P:455, ppm U:331 and ppm Th:144. § designates below detection limit of XRF (X-ray fluorescence spectroscopy).

### EXAMPLE 3

Acid extractable zirconium in the wet residue, washed with water to remove sodium salts, as prepared in Example 2, was converted to AZST by adding a calculated stoichiometric quantity of  $\text{H}_2\text{SO}_4$  thereto to form an AZST-containing product. The AZST-containing product was roasted to dryness at a temperature of about 350°C, whereafter it was dissolved in water to form an AZST-containing solution. A  $\text{Na}_2\text{CO}_3$  solution was added to about 75% of the AZST-containing solution to precipitate zirconium basic carbonate (ZBC) therefrom. The final pH of the mixture was about 6.75. The precipitated ZBC was separated from the supernatant and thoroughly washed with water until it was free of soluble sulphates. The ZBC precipitate was vigorously stirred up with the remaining 25% of the AZST-containing solution and the mixture was heated for about 10 minutes at a temperature of about 75°C, to form a ZBS-containing slurry. The ZBS-containing slurry was dried at about 150°C and purified with HCl/ $\text{HNO}_3$  solutions as described in Example 2 above. The ZBS was converted to AZST as described in Example 2 above and calcined to  $\text{ZrO}_2$  at 900° for two hours before XRF analysis. The XRF analysis for the  $\text{ZrO}_2$  is given in column e of Table II. The  $\text{ZrO}_2$  yield in this example was also about 68%.

EXAMPLE 4

AFDZ was prepared using zircon flour (95% < 45 $\mu$ m) and Na OH and the fusion or reaction conditions of Table II. The product was further treated exactly the same as was done in Example 2 up to the point before additional  
5 H<sub>2</sub>SO<sub>4</sub> is added to obtain AZST. After the acid purification washes with HCl/HNO<sub>3</sub>, the wet residue containing the in situ ZBS precipitate was oven dried, calcined at 900°C, wet milled to a d<sub>50</sub> particle size of less than 1,5 $\mu$ m and dried at about 120°C. The d<sub>50</sub> particle size of the resulting material measured 1.33 $\mu$ m with a radioactivity level of below 10 Beq/g. An opacifier test revealed  
10 opacification properties similar to that of a super fine opacifier grade marketed by the Ferro company in South Africa. An XRF analysis of the opacifier is given in Table II, column f. The mass yield for this opacifier was 83% based on the starting mass of the zircon flour used.

EXAMPLE 5

15 The efficacy of an 'inert' layer of dried water-leached comminuted AFDZ material between a mixture of zircon and alkali and interior wall surfaces of a fusion container or reactor for preventing difficulties in removing AFDZ product from the container subsequent to a fusion was tested. From experience it is known that for a zircon : alkali mass ratio of nearly 1:1 at a fusion temperature of  
20 875°C very hard fusion products result which are also cemented to the interior contact surfaces of the container to such an extent that it is very difficult to remove the fusion products from the container, especially after it has been allowed to cool down.

For the above test partitioning plate jigs were made which permitted  
25 AFDZ layer thicknesses of 3,5 and 8mm to be filled into a concentric space adjacent to vertical walls of the fusion containers of the three runs of Example 1. Bottom surfaces of the fusion containers were also filled to the same depth. The

fusion mixtures were then thrown in and tapped to rather rigid consistencies. The  
jigs were vertically withdrawn and by observation no displacement of the 'inert'  
layers appeared to have taken place. For the fusion conditions mentioned in  
Example 1 above, it was found subsequent to the fusions that all the contents of  
5 the container, even after cooling, could be easily removed by simply overturning  
the container. Only noticeable interaction between the fusion mixture and the inert  
material seemed to have taken place at a few localities in the experiment which  
used the 3mm AFDZ layer thickness.

The Applicant believes that the invention, as illustrated, provides more  
10 rapid chemical procedures for deriving zirconium products of enhanced utility  
and/or of improved purity compared to conventional methods. The processes of  
the invention maximises recovery of byproducts and significantly removes impurity  
elements, particularly iron, uranium and calcium, thus also the long lived radium  
daughters of uranium and thorium. The zircon derived base material produced by  
15 the process of the invention can be used for zirconium pigment to produce very  
acceptable colours consistently. Since the processes of the invention allows  
relatively coarse material such as zircon flour to be treated chemically to produce  
upgraded zirconium-containing products requiring only the minimum of final milling,  
the radiological problem associated with the milling of zircon to produce very fine  
20 powders, as is required for opacifier applications, can greatly be alleviated.

DATED THIS 7TH DAY OF JUNE 1999



ADAMS & ADAMS  
APPLICANT'S PATENT ATTORNEYS

